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# FINAL TECHNICAL REPORT

## Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern Recognition, and Formation/Destruction Mechanisms

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## II. Research Accomplishments (1 January 1997 – 31 December 2000)

The following is a slightly edited version of the "Accomplishments" section (and cited References) of the 3-year Renewal Proposal, submitted in February 2000, and currently supported under AFOSR F49620-01-1-0078.

The primary experimental apparatus constructed for this project is a two-chamber vacuum system which houses a pulsed, skimmed, supersonic molecular beam, equipped with three complementary detection schemes: a Surface Electron Ejection by Laser Excited Metastables (SEELEM) [SNE86ab, 88, 91] detector (with Time-of-Flight and interchangeable Au and Cs detector surface capabilities), a Germanium near-infrared (800-1700 nm) detector, and a photomultiplier (200-800 nm). This is a second-generation apparatus that was designed based on our experience with a much simpler single-chamber apparatus [HUM97]. The key feature of this apparatus is that four signal channels may be simultaneously recorded: parent molecule SEELEM (late TOF gate), metastable photofragment SEELEM (early TOF gate), infrared fluorescence excited by an ultraviolet laser (IR-LIF), and UV-LIF. This *multi-spectral* capability provides unique insights into the electronic character of the metastable species. These insights are based on a detailed and quantitative understanding of the specific characteristics of molecular eigenstates to which each detection channel is most sensitive, in other words, the "detection mechanism." In particular, each molecular eigenstate can be a mixture of several electronic states (excited singlet state,  $S_1$ , lowest triplet state,  $T_1$ , excited triplet state,  $T_i$   $i > 1$ , and electronic ground state,  $S_0$ ) and each signal channel has different detectivities for the fractional characters of each type of electronic state. Far from being spectroscopic arcanae, these fractional characters encode the chemical and photophysical properties from which fundamental excitation and decay mechanisms and practical quantitative measurements may be derived.

Any multispectral experiment will rapidly generate an enormous amount of spectral information. Advanced pattern recognition methods [COY95, 97, JAC97, 98] are essential for processing this deluge of

information. A suite of powerful pattern recognition schemes has been developed [ALT99, 00ab, CUN00b]. A key feature of these computer-automated, statistical schemes is that neither the nature nor the number of patterns being recovered from the raw multispectral data need be known in advance [JAC97, COY97]. One scheme, eXtended spectral AutoCorrelation (XAC), is designed to disentangle overlapping patterns associated with different values of the rigorously conserved upper state rotational quantum number,  $J'$  [CUN00b]. Each  $J'$  might fractionate into tens of resolved features and might overlap with the fractionated patterns belonging to several  $J'$ -values. Since each  $J'$  pattern is exactly replicated three times in a single vibronic band, via  $R(J-1)$ ,  $Q(J)$ , and  $P(J+1)$  rotational transitions, XAC is able to recover each  $J'$  pattern in a statistically rigorous manner. Once the  $J'$ -patterns are disentangled, another class of pattern recognition scheme is able to make a qualitative distinction between two extreme mechanisms of coupling between the well characterized *bright* state and the unknown manifold of *dark* states (*direct* and *doorway mediated* coupling) and to make quantitative determinations of the *dark* state molecular constants and the *bright* state-*dark* state coupling matrix elements [ALT00ab]. These computer-automated pattern recognition schemes are at least as important as the experimental apparatus in which the spectra are generated, because none of the spectra remotely resemble textbook spectra. The combination of a uniquely designed *multispectral* data set and a *statistical pattern recognition* approach provides the key to extracting information about a spectroscopic and dynamical problem of unprecedented complexity.

Although the experimental apparatus, experimental techniques, and statistical pattern-recognition methods described here are applicable to a wide range of small molecules, the following discussion applies specifically to the acetylene molecule, HCCH.

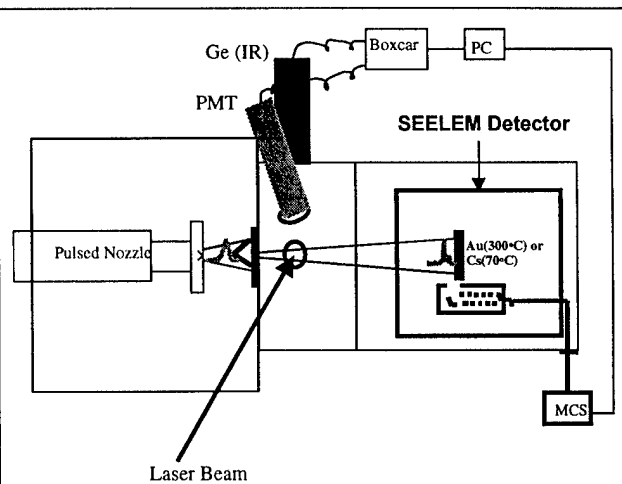
The discussion of our accomplishments during this project is organized as follows:

1. The Molecular Beam Apparatus.
2. The Mechanisms of the SEELEM and UV-LIF Detection Processes.
3. The Unexpectedly Sensitive Yet General Near Infrared Fluorescence Detection Channel.
4. Statistical Measures.
5. Dispersed Fluorescence Studies of Spectroscopic Perturbations in HCCH  $S_1$   $3v_3$ .
6. UV Cavity Ringdown.
7. Hg\* Photosensitization Experiments.
8. Collaborations at AFRL, Hanscom Research Site: Pattern Recognition and Baseline Stripping.
9. The Spectroscopic Signature of Bond-Breaking Isomerization in HCP.

## 1. The Molecular Beam Apparatus.

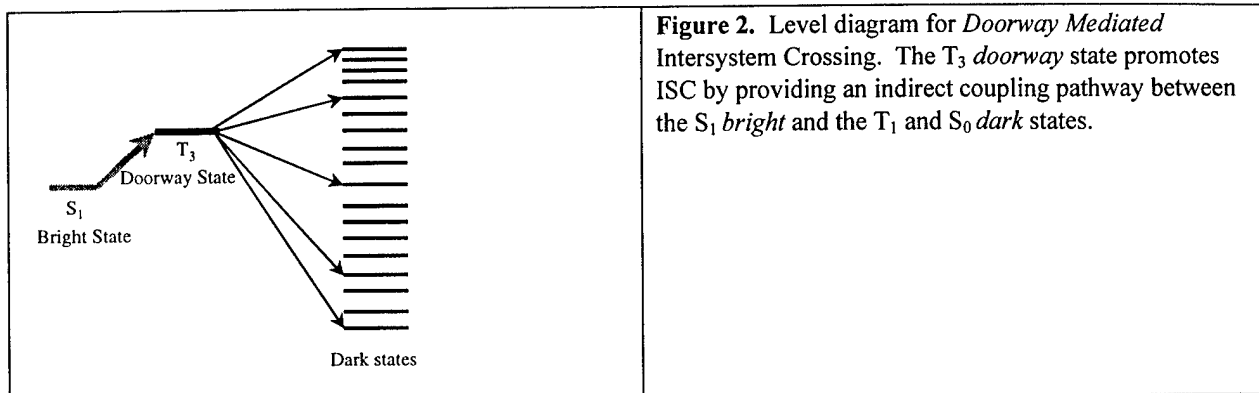
The molecular beam portion of this project began with a collaborative experiment in the laboratory of Professor Alec Wodtke at the University of California, Santa Barbara [HUM97]. The UCSB apparatus was a sophisticated and complex apparatus designed for photofragment TOF spectroscopy and the scattering of highly excited species off surfaces [MOR96]. The features of the UCSB apparatus deemed essential for the initial concept-evaluation experiments planned at MIT were incorporated into the design of a first-generation single-chamber apparatus. All of the results presented in Sections 1-5 below were obtained using the single chamber apparatus. Based on those results, a second-generation two-chamber apparatus has been designed, assembled, and is currently being tested.

**Figure 1.** Schematic of two-chamber pulsed supersonic molecular beam apparatus. The excitation region, where the UV laser crosses the molecular beam, is viewed by a PMT (UV-LIF) and a Ge IR detector (IR-LIF). Laser excited metastable molecules travel at least 3 cm before impacting the Cs or Au metal surface of the SEELEM detector. The SEELEM signal channel has Time-Of-Flight capability, which can distinguish signals due to photons, parent metastables, and metastable photofragments.



The most important feature of the metastable molecular beam apparatus is the capability of equipping the SEELEM detector with clean, heated metal surfaces of low (Cesium, 2 eV) and high (Gold, 5 eV) work function and being able to switch from one detector surface to another without altering the detector location or active area. Owing to the extreme reactivity of Cs (and the  $1 \times 10^{-4}$  Torr operating pressure of our single-chamber apparatus), the Cs surface must be continuously vacuum deposited onto a rotating disc designed so that the deposition and detection functionalities are spatially separated. The SEELEM detector (a metal plate, electron optics, and electron multiplier) is sensitive exclusively to electronically excited molecules with vertical electronic excitation energy greater than the work function of the metal surface [HAG54]. It is well established that translational and vibrational energy does not contribute to the SEELEM detectivity [LIS80]. (Vibrational excitation *can* turn on SEELEM detectivity by giving Franck-Condon access to a nuclear geometry for which the vertical electronic excitation energy is larger than the work function of the metal.) When an electronically excited molecule impacts the metal surface, an electron is ejected, collected, multiplied, and detected.

The ability to switch between two metal surfaces, with high and low work functions, enables experimental determination of the fractional composition of each SEELEM-detectable eigenstate in terms of the energetically accessible electronic states: e.g. for acetylene,  $S_1$ ,  $T_3$ , ( $T_1$ ,  $T_2$ ) (abbreviated hereafter as  $T_1$ ), and  $S_0$ . Measurement of these electronic mixing fractions is equivalent to determining the excitation, unimolecular decay, and detection mechanisms. It was our expectation that  $S_1$  and  $T_3$  *but not*  $T_1$  or  $S_0$  fractional characters would be detectable on Au, and that  $S_1$ ,  $T_3$ , and  $T_1$  characters would be detectable on Cs. In this way we expected to be able to show that the “*bright*”  $S_1$  state couples selectively to one special “*doorway*” triplet state,  $T_3$ , and that this doorway state couples to a dense manifold of background “*dark*” triplet states,  $T_1$ .



**Figure 2.** Level diagram for *Doorway Mediated* Intersystem Crossing. The  $T_3$  doorway state promotes ISC by providing an indirect coupling pathway between the  $S_1$  bright and the  $T_1$  and  $S_0$  dark states.

Furthermore, we expected to characterize this *doorway* state, thereby providing a causal (as opposed to phenomenological or statistical) mechanism for the InterSystem Crossing (ISC) [BIX67, AVO77] process in acetylene.

We discovered that, for the  $\sim 100$   $\mu$ s transit times from the laser excitation region to the SEELEM detector surface, the Au and Cs surfaces are both primarily sensitive to  $S_1$  and not  $T_3$  character. This is a surprising result, with fundamental implications about the SEELEM detection process (both mechanism and quantum efficiency) in molecules (see Section 2, below) [SNE88]. Despite the unexpectedly low sensitivity of the SEELEM detector to triplet vs. excited singlet character, we were able to infer the fractional  $S_1$  and  $T_3$  characters in SEELEM-detectable eigenstates by exploiting the quite different dependence on  $S_1$  character of the SEELEM vs. UV-LIF detection channels. This enabled us to demonstrate that ISC in HCCH  $S_1$  is **Doorway Mediated** and to determine the properties of the *doorway* state.

We also know, by significantly increasing the transit time from excitation region to SEELEM detector surface, that it will be possible to determine the  $S_1$  vs.  $T_3$  relative sensitivities on Au and Cs surfaces and, by comparing SEELEM spectra recorded on Au and Cs, to measure directly the fractional  $T_3$  and  $T_1$  characters in the detected eigenstates. In order to compensate for the much higher sensitivity to  $S_1$  than triplet character, it is necessary to ensure, by a long flight time from excitation to detector, that the only metastable molecules reaching the detector are those with fractional  $S_1$  character a factor of at least 10 smaller than triplet character. Our second-generation apparatus has been designed with the possibility of varying the excitation to detector transit time from 20  $\mu$ s (3 cm in a He beam) to 1400  $\mu$ s (81 cm in an Ar beam), which is to be contrasted with minimum and maximum transit times of 80 and 200  $\mu$ s in our first-generation apparatus.

The first-generation apparatus is an unskimmed pulsed jet. The jet is crossed by the excitation laser 1 cm downstream from the nozzle. The excitation region is imaged ( $f/2$  optics) onto a photomultiplier for detection of UV-LIF. Since near-IR-LIF turned out to be unexpectedly intense, we improvised an optical system ( $\sim f/10$  optics) for imaging IR-LIF from the excitation region onto a liquid  $N_2$  cooled Ge detector. The SEELEM detector is located  $\sim 12$  cm downstream from the excitation region. The signal from the SEELEM detector consists of as many as three temporal features: UV fluorescence (and laser scatter) at  $\sim 0$  delay, *metastable photofragments* at early time, and metastable parent molecules at later time [HUM97]. The carrier of the metastable photofragment signal is unknown (but most likely a  $>5$  eV excited metastable state of CCH), but its formation from unexcited acetylene requires absorption of at least two 5.5 eV UV photons!

The SEELEM-TOF spectrum, in principle, contains information about the distribution of radiative lifetimes of the SEELEM-detectable eigenstates. However, this information is corrupted by two instrumental artifacts that cause a rapid decay, during each molecular beam pulse, in the intensity of the parent metastable feature of the TOF-SEELEM signal. These artifacts, which provide the primary motivation for redesign of the apparatus, are due to (i) attenuation and heating of the unskimmed molecular jet by the buildup of background gas scattered off the SEELEM detector surface, and (ii) reduced efficiency of the SEELEM surface during each gas pulse owing to inter-pulse reversible contamination by the enormous flux of molecules from the jet. There is, however, also the unevaluated effect on the SEELEM detector quantum efficiency due to steady-state surface contamination at the  $1 \times 10^{-4}$  Torr working pressure.

One of the most surprising results from the single-chamber apparatus is that the SEELEM spectra recorded on Au (5 eV work function) and Cs (2 eV work function) are essentially identical. The simplest explanation of this result, which is independently confirmed by statistical measures applied to simultaneously recorded SEELEM and UV-LIF spectra, is that both Au and Cs surfaces are vastly more sensitive to  $S_1$  than triplet character. Experiments carried out during 2001 show that adsorbed acetylene shuts down triplet detectivity.

The second-generation apparatus consists of two (source and detector) independently pumped chambers, a new pulsed nozzle with a 35  $\mu$ s FWHM open time, a skimmer located  $\sim 1$  cm (adjustable) downstream from the nozzle, the distance from excitation region to SEELEM surface variable from 3 to 48 cm (plus an additional 33 cm with addition of an auxiliary chamber), beam-on pressure in the detector chamber of  $4 \times 10^{-6}$  Torr (in contrast to  $1 \times 10^{-4}$  Torr with the nozzle operated at 10 Hz in the original apparatus), optimized  $f/2$  optics for both IR-LIF and UV-LIF, and an IR detector (same  $D^*$  as the previous IR detector) with a response time (8  $\mu$ s now vs. 100  $\mu$ s previously) sufficiently fast to measure the radiative lifetime of the unknown carrier of the IR-LIF signal (most likely the  $\tilde{A}$ -state of CCH). The improved collection optics and IR detector response should increase the IR-LIF signal by a factor of  $\sim 50$ . The use of a skimmed jet will reduce the Doppler widths of the IR-LIF and UV-LIF channels to  $\sim 0.003$   $\text{cm}^{-1}$ , which in turn motivates replacement of our pulsed dye laser by an available pulse-amplified, cw tunable laser system.

## 2. The Mechanisms of the SEELEM and UV-LIF Detection Processes.

The SEELEM signal strength is given by the product of three factors: excitation probability, probability that the molecular excitation survives through the transit time from laser excitation to impact on the SEELEM surface, and probability of ejection of an electron from the detector surface [HUM97]. The SEELEM signal that results from excitation of the  $j$ -th eigenstate will depend on the specific admixture of electronic-vibrational basis states in that eigenstate:

$$|j\rangle = \alpha|S_1, v\rangle + \sum_i \beta_i|T_3, v_i\rangle + \sum_i \gamma_i|T_1, v_i\rangle + \sum_i \delta_i|S_0, v_i\rangle \quad (1)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are mixing coefficients which express the respective contributions of  $S_1$ ,  $T_3$ ,  $T_1$ , and  $S_0$  electronic states to the mixed eigenstate and the subscript  $i$  labels the vibrational level of the corresponding electronic state. All of the mixing coefficients are real, and

$$1 = |\alpha|^2 + \sum_i \left[ |\beta_i|^2 + |\gamma_i|^2 + |\delta_i|^2 \right] \quad (2)$$

Since the electronic ground state is a singlet,  $S_0$  (total electron spin  $S = 0$ ), and electronic transitions between singlet and triplet (total electron spin  $S = 1$ ) states are forbidden, only the  $S_1 \leftarrow S_0$  transition is allowed and the  $S_1$  basis state is called the “*bright state*.” All of the other basis states, because they can neither be excited from  $S_0$  nor decay into  $S_0$  by spontaneous fluorescence, are called “*dark states*”. The  $T_3$  state is a special triplet state because it is a more highly excited electronic state than  $T_1$ . Because  $T_3$  is more highly excited than  $T_1$ , the density of vibrational levels associated with the  $T_3$  electronic state ( $\sim 1$  per 100  $\text{cm}^{-1}$ ) is much smaller than that associated with  $T_1$  (10 per  $\text{cm}^{-1}$ ) at the energy of the initially prepared  $S_1$  *bright state*. Therefore, it is common to consider only one  $T_3$  vibrational level as contributing significantly to the  $j$ -th eigenstate, and this unique  $T_3$  vibrational level *might* have special dynamical significance. It is called the “*Doorway State*” because it *could* play a promoter role in the coupling between  $S_1$  and the dense manifold of dark states,  $T_1$  and  $S_0$ . Therefore, in what follows, mixing coefficients for only one  $S_1$  ( $\alpha$ ) and one  $T_3$  ( $\beta$ ) basis state will be considered in Eqs. (1 and 2).

The three multiplicative factors that give the relative intensity of a transition terminating on the  $j$ -th eigenstate in a SEELEM spectrum are:

$$\text{Excitation Probability} = I S_{J',J''} N_{J''} \alpha^2 \quad (3a)$$

$$\text{Survival} = e^{-[\alpha^2 \Delta t / 0.27]} \quad (3b)$$

$$\text{Electron Ejection} = \left[ \alpha + \theta_3 \beta + \theta_1 \sum_i \gamma_i \right]^2 \quad (3c)$$

where  $I$  is the laser intensity,  $S_{J',J''}$  is the rotational linestrength (Hönl-London factor),  $N_{J''}$  is the population of the lower level of the transition,  $\Delta t$  is the flight time (in  $\mu\text{s}$ ) from excitation to detector plate,  $0.27 \mu\text{s}$  is the radiative lifetime of a pure  $S_1$  basis state [OCH87, 91, ABE93], and  $\theta_3$  and  $\theta_1$  are unknown factors that express the *amplitude* detectivities of  $T_3$  and  $T_1$  relative to  $S_1$ . Notice that, although the first and third factors increase as the fractional  $S_1$  character increases, one can have too much of a good thing. The survival factor typically prohibits SEELEM detection of eigenstates with more than  $\sim 1.4\%$   $S_1$  character ( $\tau < 2 \times 10^{-5}$  s). Our original expectation was that the relative detectivities of  $S_1$  and  $T_3$  on Au and of  $S_1$ ,  $T_3$ , and  $T_1$  on Cs would be nearly identical ( $\theta_3$  and  $\theta_1 \approx +1$  or  $-1$ ). This would have greatly facilitated direct experimental measurement of the fractional  $T_3$  and  $T_1$  characters and also have led to a factor of  $\sim 1000$  enhancement of the SEELEM intensity on Cs relative to that on Au! The expected 1000-fold enhancement on Cs reflects the  $T_1:T_3$  ratio of vibrational densities of states at the 5.5 eV energy of the  $S_1$   $3v_3$  bright state. However, despite the well documented triplet-dominated sensitivity of SEELEM detectors to eigenstates with fractional singlet character ( $\alpha^2$ ) less than 0.01% [LIS80, SNE88, 91], the SEELEM spectra recorded in our first-generation apparatus are compatible with *zero* sensitivity to triplet character. There is a fundamental reason why the SEELEM process should be more sensitive to  $S_1$  than triplet character and the sensitivity to triplet character should be more rapidly degraded by contamination [HAG54]. Recent experiments on a clean Cs surface yielded the predicted 1000-fold enhancement over the Au surface.

Two distinct physical processes contribute to the SEELEM effect [HAG54]: (i) an electron is ejected from the metal surface when the molecule transfers its electronic excitation energy to the surface via a long-range interaction between the molecular transition dipole moment and the image dipole moment in the surface [CHA78]; (ii) an electron is ejected from the molecule when, via orbital overlap at short-range, an electron is transferred from the metal surface into a vacancy in the lowest lying unfilled molecular orbital. The first process is exclusively sensitive to  $S_1$  character and relatively robust with respect to surface contamination; the second is comparably sensitive to  $S_1$  and T characters but rapidly



degraded by molecules adsorbed on the detector surface. Both processes require that the vertical electronic de-excitation energy in the molecule is larger than the work function of the metal.

The product of three factors also gives the relative intensities of transitions in the UV-LIF spectrum:

$$\text{Excitation Probability} = I S_{J', J''} N_{J''} \alpha^2 \quad (4a)$$

$$\text{Non - flyout} = (1 - e^{-\alpha^2 \delta t / 0.27}) \quad (4b)$$

$$\text{PMT Cathode Efficiency} = f(\lambda) \quad (4c)$$

where the excitation probability factor is identical to that for the SEELEM spectrum,  $\delta t$  is the time required for the excited molecule to travel out of the PMT field of view, and  $f(\lambda)$  is the wavelength-dependent PMT cathode sensitivity. The survival factor in the SEELEM expression (Eq. 3b) and the Non-flyout factor in the UV-LIF expression (Eq. 4b) result in a near complementarity of the SEELEM and UV-LIF channels; eigenstates that are SEELEM detectable ( $\tau > 20 \mu\text{s}$ ,  $\alpha < 0.12$ ) are not UV-LIF detectable and *vice versa* ( $\tau < 3 \mu\text{s}$ ,  $\alpha > 0.30$ ).

Previous studies of the SEELEM effect (often called the “Auger effect” [HAG54, LIS80], but this name has acquired a completely different connotation in Surface Science) in atoms and diatomic molecules have been unable to explore the relative strengths of and quantum interferences between the contributions from multiple electronic states to SEELEM signals [HAG54, LIS80, SNE86ab, 88, 91]. Acetylene is unique in the possibility that two ( $S_1$  and  $T_3$ ) electronic states potentially contribute to the SEELEM effect on Au and three ( $S_1$ ,  $T_3$ , and  $T_1$ ) on Cs. Acetylene is also unique in that its vibronic density of states is sufficiently low (neglecting interaction with  $S_0$ ) that individual eigenstates can be resolved in both SEELEM and LIF spectra, and that a complete model for the interactions among these states can be inferred from the totality of spectroscopic observations [DRA94, OCH87, 91, DUP91, 93, 95ab, HUM97]. Our multispectral studies of acetylene will determine the signs and magnitudes of the amplitude detectivity factors in Eq. 3c, thereby providing fundamental insights into the mechanism of the SEELEM effect and the factors that determine the quantum efficiency of SEELEM detection on various metal surfaces. In turn, a fundamental understanding of the SEELEM effect, in particular of the interference effects among several electronic states in a mixed eigenstate, in combination with the high resolution multispectral data sets recorded in our second-generation apparatus, will yield qualitatively new insights into the mechanisms of Intersystem Crossing and Internal Conversion in small polyatomic molecules [BIX67, AVO77, STA81, NES96].

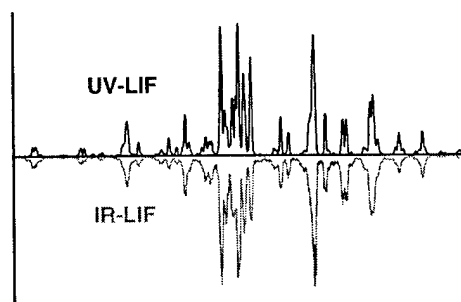
### 3. The Unexpectedly Sensitive Yet General Near Infrared Fluorescence Detection Channel.

We first observed near infrared fluorescence resulting from UV laser excitation of acetylene in static gas cell experiments [DRU97]. Careful examination of the laser intensity dependence of the IR signal suggests that most of the IR fluorescence is due to a multiphoton process that produces an unknown electronically excited photofragment of acetylene. This multiphoton process is enhanced at the one-photon level by resonance with an eigenstate of predominant  $S_1$   $3v_3$  character. In the static gas cell experiment, the nearby  $S_1$   $4v_b$  perturber levels (four quanta of nontotally symmetric bending vibration [SCH86, UTZ93, CUN00a]) did not contribute significantly to this multiphoton process.

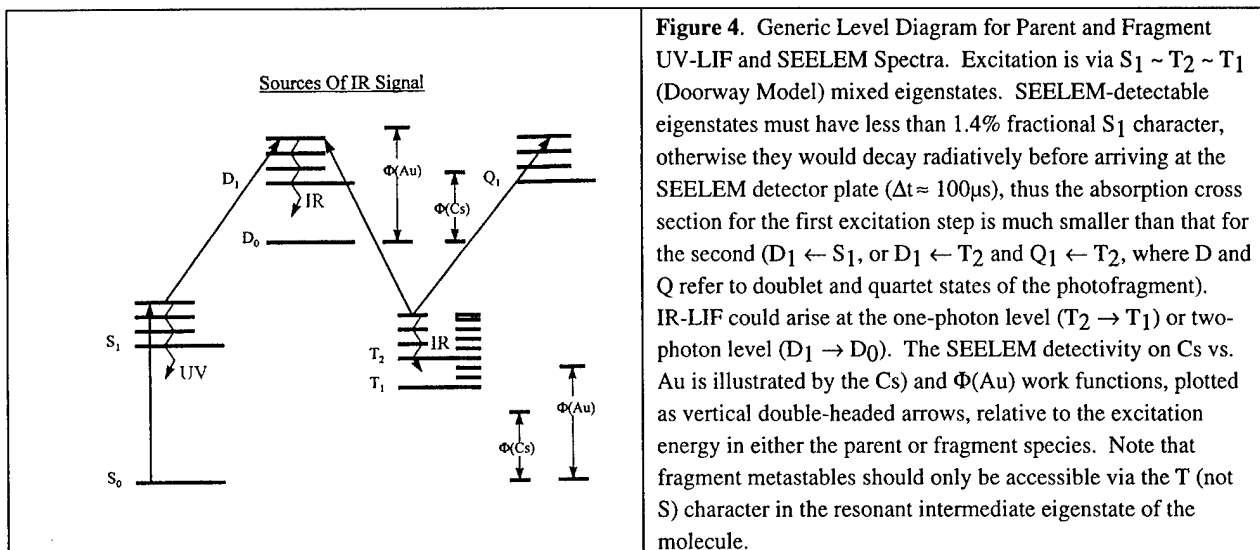
In a serendipitous and improvised (sub-optimal  $\sim f/10$  light collection and too slow 100  $\mu\text{s}$  time response of the IR detector) experiment, we discovered that the near-IR-LIF signal in our first-generation molecular beam apparatus is respectively stronger than the SEELEM signal and comparable to the UV-LIF

signal and nearly identical in spectral pattern to that in the UV-LIF channel (Figure 3). This implies that the quantum yield (signal counts per absorbed UV photon) for two-photon excitation of an infrared-emitting photofragment must be at least comparable to that for direct, one-photon excitation of UV-LIF detectable acetylene molecules. The solid angle of the SEELEM detector is such that all molecules in the jet, which pass through the UV-laser excitation region, will strike the active area of the SEELEM detector. However, we have crudely measured the quantum efficiency for SEELEM detection to be  $\sim 5 \times 10^{-6}$ , much smaller than the quantum efficiency of the infrared detector. The product of detector solid angle and efficiency factors for SEELEM vs. IR-LIF detection favors IR-LIF by a factor of  $\sim 100$ , which implies that the strengths of the two excitation pathways will be comparable at UV laser pulse intensities only slightly larger than the unfocussed 100  $\mu\text{J}$  currently in use. We believe that this is not an accident and that the resonance enhanced, multiphoton IR-LIF channel will be an unexpectedly sensitive detection channel for characterizing metastable states and Intersystem Crossing in many small polyatomic molecules which have a multiple bond.

**Figure 3.** Comparison of UV-LIF (upward) and IR-LIF (downward) spectra in the region of the  $S_1$   $3\nu_3$  level.



In acetylene, a single  $\pi^* \leftarrow \pi$  orbital excitation produces the  $S_1$  and  $T_{1,2,3}$  excited states [ING53, INN54, PRI45, KAM70, DEM75, WET78, SEK85, LIS86, VAC93, YAM93, 94, STA94, SHE96, CUI96]. A second orbital excitation would nominally lead to a CCH photofragment with a hole in the  $\pi$  orbitals or a singly occupied  $\pi^*$  orbital or both. These correspond to electronically excited states of CCH. If the excited state is a doublet state ( $S=0.5$ ), then the excited state could decay by near infrared fluorescence analogous to the  $\text{CN } A^2\Pi \rightarrow X^2\Sigma^+$  transition. If the excited state is a quartet state ( $S=1.5$ ), it would be sufficiently long-lived and energetic to be SEELEM detectable. The metastable photofragment that was observed in the TOF-SEELEM spectrum in the region of  $S_1$   $4\nu_3$  [HUM97] *could* be a quartet state of CCH.



**Figure 4.** Generic Level Diagram for Parent and Fragment UV-LIF and SEELEM Spectra. Excitation is via  $S_1 \sim T_2 \sim T_1$  (Doorway Model) mixed eigenstates. SEELEM-detectable eigenstates must have less than 1.4% fractional  $S_1$  character, otherwise they would decay radiatively before arriving at the SEELEM detector plate ( $\Delta t \approx 100 \mu\text{s}$ ), thus the absorption cross section for the first excitation step is much smaller than that for the second ( $D_1 \leftarrow S_1$ , or  $D_1 \leftarrow T_2$  and  $Q_1 \leftarrow T_2$ , where D and Q refer to doublet and quartet states of the photofragment). IR-LIF could arise at the one-photon level ( $T_2 \rightarrow T_1$ ) or two-photon level ( $D_1 \rightarrow D_0$ ). The SEELEM detectivity on Cs vs. Au is illustrated by the Cs and  $\Phi(\text{Au})$  work functions, plotted as vertical double-headed arrows, relative to the excitation energy in either the parent or fragment species. Note that fragment metastables should only be accessible via the T (not S) character in the resonant intermediate eigenstate of the molecule.

It is reasonable to expect, for a large and important class of unsaturated polyatomic molecules, that sequential excitation processes, via *either the low- $\nu$   $S_1$  or low- $\nu$  T* character of one-photon excited eigenstates, will *generally* give rise to a near IR fluorescence signal that is of comparable intensity to the SEELEM signal. It is important to note that the information in the SEELEM and IR-LIF channels is complementary. SEELEM detectivity should be independent of T vibrational state (neglecting mode-specific fractionation of T into  $S_0$ ), whereas the IR-LIF channel depends on Franck-Condon overlap and energy match with a predissociated, gerade-Rydberg vibronic final state at the two-photon level [ASH87, TAK92].  $S_1$  and T basis states of low vibrational excitation (in which one turning point resembles the equilibrium geometry of the final dissociative state) should dominate the IR-LIF signal channel, provided that the UV photon is resonant with the g-Rydberg  $\leftarrow (T, S_1)$  transition. In contrast, of those molecules that absorb one photon, only a small fraction will escape all of the fates antithetical to SEELEM detection: absorption of a second photon followed by rapid radiative decay or dissociation into electronically unexcited photofragments, rapid UV fluorescence decay of the one-photon excited eigenstate prior to impact on the SEELEM detector (too much  $S_1$  character), and failure of the one-photon excited eigenstate to eject an electron from the SEELEM detector (too little  $S_1$  character).

IR-LIF spectra were recorded in the region of the HCCH  $S_1$  zero-point level, which is also the predicted energy region [CUI96, SHE96, VAC93, 96] of the minimum energy half-linear point on the  $T_2$  potential energy surface. Three vibrational bands, the acetylene  $S_1 \leftarrow S_0$  origin band and two  $S_1(1\nu_3) \leftarrow S_0(2\nu_4)$  hot bands, are observed in both UV-LIF and IR-LIF channels, but the *hot bands* were  $\sim 50$  times *stronger* in the IR-LIF than UV-LIF channel. This observation is the basis for our claim that Franck-Condon and energy match factors determine IR-LIF intensities.

Calculations [CUI96] suggest that  $T_2 \sim T_1$  spin-orbit interactions are much weaker than the  $T_3 \sim T_2$  and  $T_3 \sim T_1$  interactions. This is supported by Kanamori's [KAN98] observation of negligible fractionation of the upper level of the  $T_2(\text{cis}) \leftarrow T_1(\text{cis})$  origin band. Therefore we expect that, below the energy of the  $T_3$  zero-point level, the  $T_2$  vibrational levels will be sufficiently free of fractionation into high vibrational levels of  $S_0$  that several vibrational levels of the  $T_2$  state (especially overtones of the *trans*-bend in the *trans*-bent isomer and overtones of the *cis*-bend in the *cis*-bent isomer) should be observable in the IR-LIF spectrum. On the other hand, we do not expect to see transitions into the denser manifold of  $T_1$  vibrational levels in the  $S_1$  origin band region of the IR-LIF spectrum, because those states are too highly excited (and

extensively mixed by anharmonic resonances) to have appreciable Franck-Condon overlap with the final (linear geometry) state that dissociates into the IR-emitting photofragment. Our IR detector failed just after our initial unsuccessful attempt to record  $T_2 \leftarrow S_0$  IR-LIF spectra. The first-generation apparatus was dismantled and the second-generation molecular beam apparatus was designed to optimize the IR-LIF detection channel.

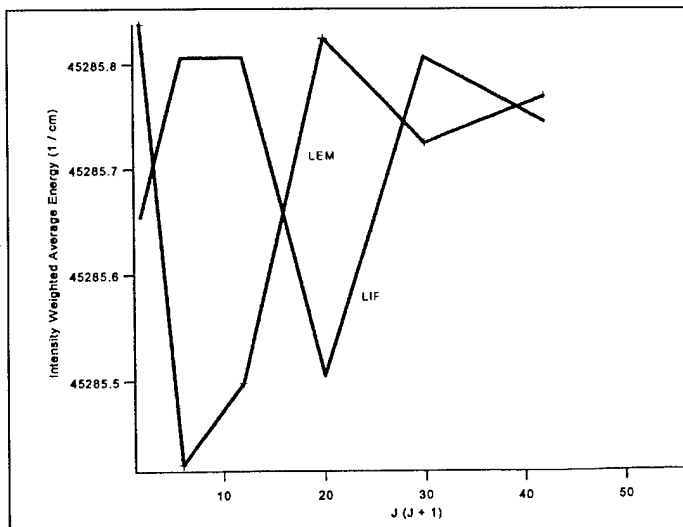
$T \leftarrow S_0$  transitions in H, C, N, O molecules are extremely weak. Previous efforts to detect such transitions have focussed on detection of extremely weak phosphorescence (direct or sensitized [SUZ97, PRA88]) or SEELEM signals from metastable parent molecules. Multiphoton photofragmentation processes will frustrate attempts to enhance the intensity of such parent-metastable-based signals by increasing laser intensity. Since the transition moment for the  $T \leftarrow S_0$  transition will be enormously smaller than those for all subsequent  $T' \leftarrow T$  transitions, a very small fraction of the molecules excited from  $S_0$  will survive the excitation pulse as intact parent metastable molecules. The IR-LIF detection scheme, which is intrinsically a multiphoton photofragmentation process, will be far more robust and generally applicable than the parent molecule phosphorescence and SEELEM detection schemes!

#### 4. Statistical Measures.

A central goal of this project is to gain information about a large and poorly understood class of long-lived, energetic, and non-fluorescing molecular states that cannot be obtained by known spectroscopic techniques. Such a goal inevitably requires uncovering and dealing with unprecedented spectral complexity. We have built an apparatus with which we have demonstrated the capability to record enormous multispectral TOF-SEELEM/UV-LIF/IR-LIF data sets. It would be naïve to expect that these data could be directly input into a least-squares-fitting routine that is based on a standard spectroscopic effective Hamiltonian model [LEF86]. Moreover, standard spectroscopic models are likely to be prohibitively opaque when applied to energy regions where the vibrational density of states approaches 10 per  $\text{cm}^{-1}$ .

We have devised several kinds of statistical pattern recognition schemes to deal with the unique problems posed by the data sets we are now capable of recording [COY95, 97, JAC97, ALT99, 00ab, CUN00b].

Whenever a dynamical quantity is conserved (either rigorously, as for a symmetry-based good quantum number, or approximately, as defined by the finite time that corresponds to the resolution of the spectrum), that conserved quantity will give rise to a pattern that is exactly repeated in the spectrum. The difficulty that must be overcome is that the patterns associated with different values of the conserved quantity (e.g. the rotational quantum number,  $J$ ) often overlap each other and these overlapping patterns must be disentangled, without benefit of any prior knowledge about the nature of the patterns. We have developed powerful spectral autocorrelation and cross-correlation methods [JAC97, COY97, CUN00b] and applied them to a variety of problems [JAC98, VIT97a-g].



**Figure 5.** Intensity weighted average energies, extracted by the XAC pattern recognition scheme, from extensively overlapped fractionated  $J'$ -patterns in UV-LIF and SEELEM spectra in the region of  $S_1$   $3\nu_3$ . With the exception of the  $J'=4$  point, the  $J'$ -sorting procedure is perfect, and the UV-LIF spectrum yields the horizontal straight line required by perturbation theory, with scatter on the order of the  $0.08 \text{ cm}^{-1}$  resolution. The larger deviations, at  $J=2$  and  $3$  in the SEELEM spectrum, are genuine and constitute proof that the S-T coupling is *Doorway-Mediated* rather than *Direct* and that the  $T_3$  doorway state overtakes  $S_1$  from below at  $J=3$ .

Figure 5 displays intensity weighted average rotational energy plots obtained from the UV-LIF and SEELEM spectra of the acetylene  $\tilde{A} - \tilde{X} \quad V_1^3 \quad K_1^0$  hot band by the eXtended spectral AutoCorrelation (XAC) method. The sorting of the spectra into separated patterns associated with each of the upper state  $J'$ -values is satisfactory, but would be improved if the spectra could be recorded at higher resolution and signal:noise ratio. Significantly, we observed that an improvement in UV laser resolution ( $0.2 \text{ cm}^{-1}$  at UCSB [HUM97],  $0.08 \text{ cm}^{-1}$  at MIT [ALT98, CUN00b]) led to a dramatic S:N improvement. We plan to increase the laser resolution from the present  $\sim 0.08 \text{ cm}^{-1}$  FWHM Nd:YAG pumped, frequency doubled, pulsed dye M to  $\sim 0.003 \text{ cm}^{-1}$  by replacing our laser by a frequency doubled, pulse-amplified, cw-doubled, Ti:sapphire laser (Coherent 899-29, supplied by DURIP Grant F499620-97-1-0245) during the requested grant period.

Another kind of pattern serves as the unique signature of two qualitatively opposite mechanisms of Intersystem Crossing: the "*Doorway Mediated*" and "*Direct*" models [AVO77, ALT00ab]. In the *Doorway* model, there is one *bright* state ( $S_1$ ), one *doorway* state ( $T_3$ ), and a dense manifold of *dark* states ( $T_1, S_0$ ). The *bright* state is bright because it is connected to thermally populated levels of the ground electronic state by an electric dipole allowed transition. The *doorway* and *dark* states are dark because they can neither be excited from the ground state nor decay by emission of detectable fluorescence. The *doorway* state is special, acting as a promoter of Intersystem Crossing because it is coupled by off-diagonal spin-orbit matrix elements to *both* the *bright* and *dark* states. In the *Doorway* model the *bright* state has no direct off-diagonal matrix elements to the *dark* states. In the *Direct* model, there is no special promoter or *doorway* state; the *bright* state has nonzero off-diagonal matrix elements to all *dark* states.

Since the statistical measures used to distinguish qualitatively between the *Doorway Mediated* and *Direct* models also serve to determine quantitatively the molecular constants of the *doorway* state and the *bright-doorway* state coupling matrix element [ALT00ab], both the qualitative and quantitative capabilities of each statistical measure are discussed here. The statistical measures are:

(i) Mean Energy. 
$$E_{ave} = \sum I_i E_i \quad (5)$$

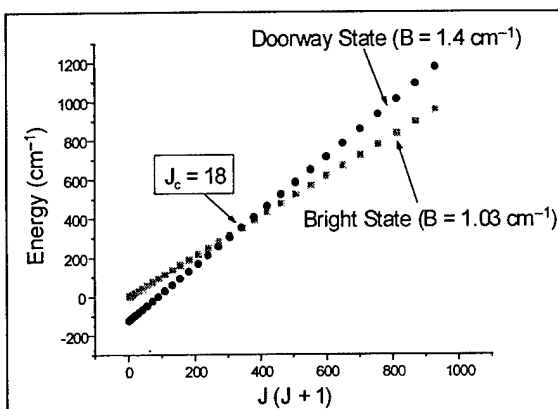
(ii) Skewness 
$$S = \sum_i I_i^2 [E_i - E_{ave}] \quad (6)$$

(iii) Correlation. 
$$C_{\Delta v} = \frac{\sum_i [I_i^{LIF} * I_i^{LEM}]_{\Delta v}}{\sum_i [I_i^{LIF}]^2} \quad (7)$$

(iv) Fractionation. 
$$F = \sum_i I_i^2 \quad (8)$$

(v) Lawrance-Knight De-Diagonalization [BER76, LAW85, 91, LEH91].

$I_i$  is the intensity in the  $i$ -th resolution element of a spectrum,  $E_i$  is the energy that corresponds to the  $i$ -th resolution element,  $E_{ave}$  is the intensity weighted energy averaged over all resolution elements in a spectrum (e.g. SEELEM, UV-LIF, or IR-LIF) which belong to the same value of the rigorous quantum numbers (e.g.  $J'$  and parity), and  $[I_i^{LIF} * I_i^{LEM}]_{\Delta v}$  is the product of intensities in LIF and SEELEM spectra calculated at resolution  $\Delta v$ .



**Figure 6.** Schematic of a level crossing between a *bright* state ( $S_1$ ) and a *doorway* state ( $T_3$ ). The level crossing occurs at  $J_c = 18$  rather than at  $J_c = 3$  as observed in the spectrum of  $S_1 3v_3$

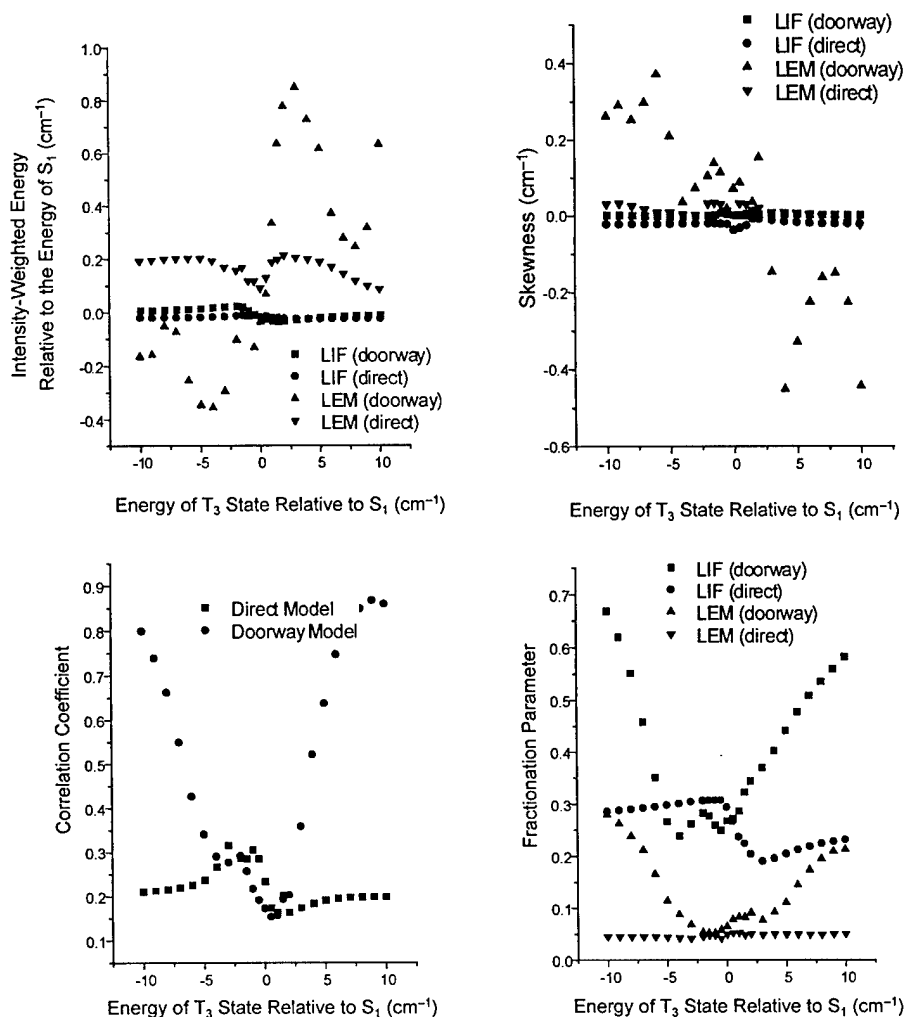
A good framework for understanding the information revealed by each of the statistical measures is to imagine, for the *Doorway Mediated* model, that the *bright* and *doorway* basis states have slightly different rotational constants and vibrational energies such that, on an energy vs.  $J(J+1)$  plot, the straight line of slope  $B_{bright}$  intersects the straight line of slope  $B_{doorway}$  at  $J_c$ . At the level crossing,  $J_c$ , the resultant eigenstates exhibit the largest level-shifts from the unperturbed basis state energies and also the largest *bright-doorway* mixing coefficients. Also, a sign-reversal of mixing coefficients and quantum interference effects occurs on opposite sides of  $J_c$  [LEF86]. If the coupling is *Direct* rather than *Doorway Mediated*, then there will be no sign of a level crossing nor, for any value of  $J'$ , any sign of asymmetries in the various spectra associated with a *doorway* state either above or below the *bright* state.

(i) Mean Energy. In the UV-LIF spectrum, the  $J'$ -dependence of  $E_{ave}$  is indistinguishable from the energy of the *bright* state for both *Direct* and *Doorway* models [ALT00a]. This is useful because it provides a simple and accurate method for extracting the molecular constants of the *bright* state from a complicated UV-LIF spectrum provided that the  $J'$ -sorting procedure is successful. In a *Doorway* model SEELEM spectrum, the  $J'$ -dependence of  $E_{ave}$  exhibits a strong asymmetry, which locates  $J_c$  and for each- $J'$  determines whether the *doorway* state lies above or below the *bright* state. In a *Direct* model SEELEM spectrum, there is an approximately constant offset of  $E_{ave}$  from the energy of the bright state.

(ii) Skewness. Only the *Doorway* model SEELEM spectrum exhibits skewness [ALT00a]. The skewness is zero at  $J_c$  and the sign of the skewness determines whether the *bright* state lies above or below the *doorway* state.

(iii) Correlation. The correlation depends strongly on  $\Delta v$ , approaching zero as  $\Delta v$  goes to zero. For the *Doorway* model, at finite resolution, the correlation increases from nearly zero at  $J_c$  to near unity at  $J'$  values above and below  $J_c$ . For the *Direct* model, the correlation is small and essentially independent of  $J'$  [ALT00a].

(iv) Fractionation [HEL97, NES96]. The fractionation index can range from 1 (no fractionation) to  $1/N$  (maximum fractionation), where  $N$  is the number of potentially interacting states. The *Doorway* model exhibits a characteristic non-symmetric fractionation pattern with minimum fractionation index (approximately equal to the roughly constant value for the *Direct* model) near  $J_c$  in both UV-LIF and SEELEM spectra. The absence of reflection symmetry about  $J_c$  is due to quantum interference between  $S_1$  amplitudes obtained directly and via the  $T_3$  (*doorway*) perturber [ALT00a].



**Figure 7.** Summary of four statistical measures applied to *Doorway Mediated* and *Direct Model* spectra [ALT00a]. The patterns shown here illustrate the qualitative differences between *Doorway Mediated* and *Direct Model* behavior and also show how quantitative molecular constants for the *Doorway* state may be obtained without a full fit of eigenstates to an  $H^{\text{eff}}$  model.

(v) Lawrance-Knight De-Diagonalization. The Lawrance-Knight (L-K) method, originally proposed by Berg [BER76], later reformulated by Lawrance and Knight [LAW85, 91], and critiqued by Lehmann [LEH91], permits exact inversion of a spectrum (frequencies and relative intensities) to a special

kind of zero-order model (one bright state coupled to a “prediagonalized” manifold of dark states), which is identical to our *Direct* model. One obtains the deperturbed energies of the *bright* and *dark* states and the values of the coupling matrix elements between the *bright* state and each *dark* state. When the L-K method is intentionally applied to the *Doorway* model case (for which it was explicitly not intended), one obtains information (from the skewness of the L-K output) about the location of the *bright* state  $\sim$  *doorway* state level crossing,  $J_C$ , whether the *bright* state is crossed by the *doorway* state from above ( $B_{\text{bright}} > B_{\text{doorway}}$ ) or below, and the magnitude of the *bright*  $\sim$  *dark* coupling matrix element [ALT00b].

The L-K procedure is the most powerful of all the statistical measures we have examined, both for qualitatively distinguishing between *Doorway* and *Direct* model coupling cases and for quantitatively determining the molecular constants that describe the *doorway* state and the *bright*  $\sim$  *dark* coupling matrix element. Its value as a spectroscopic tool is illustrated by the following example where we were forced to revise our original model for the SEELEM detection process [ALT00b].

Equation (3c) gives the probability of ejection of an electron from the metal surface of the SEELEM detector. The form of this expression, where an event probability is given by the square of a sum of amplitudes, is demanded by fundamental postulates of Quantum Mechanics. However, the signs and magnitudes of the  $\theta_1$  and  $\theta_3$  factors are dependent in an unknown way on the electronic wavefunctions of the various molecular electronic states and the metal surface. We assumed initially that both  $\theta$  factors are approximately +1 or -1. When we make this assumption, several inconsistent conclusions are drawn from UV-LIF and SEELEM spectra. The L-K skewness measure, applied to the high resolution UV-LIF spectrum recorded by Drabells et al. [DRA94] implies that the  $T_3$  *doorway* state starts out below the  $S_1$   $3v_3$   $K'=1$  *bright* state at  $J'=1$  and crosses the *bright* state at  $J_C=3$ . The skewness statistic defined by Eq. 6, applied to the  $S_1$   $3v_3$   $K'=1$  *bright* state SEELEM spectrum, implies that the *doorway* state starts out above the *bright* state at  $J'=1$ . However, when  $\theta_3$  is reduced from 1 to 0.01, the sense of the SEELEM skewness is reversed and the statistical analyses of the SEELEM and UV-LIF spectra give consistent results [ALT99, 00b]. A much reduced detectivity factor for triplets relative to  $S_1$  also explains the absence of any significant differences between both the shapes and the relative intensities of the SEELEM spectra recorded on Au (where  $T_3$  is in principle detectable) and Cs (where both  $T_3$  and  $T_1$  are in principle detectable). It is plausible that the Au/Cs invariance of the SEELEM spectra is due to contamination of the Cs surface, because SEELEM detection of triplet states requires a shorter-range interaction between molecule and metal surface than does detection of singlet states [CHA78].

## 5. Dispersed Fluorescence Studies of Spectroscopic Perturbations in HCCH $S_1$ $3v_3$ .

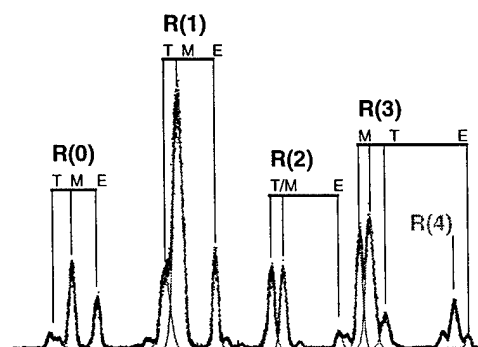
Spectroscopic perturbations are windows through which one can view otherwise unobservable classes of electronic-vibration states [LEF86] and, most significantly yet least appreciated, the *causal mechanisms* (in contrast to phenomenological rates) of dynamical processes such as Intramolecular Vibrational Redistribution (IVR), Intersystem Crossing (ISC), and Internal Conversion (IC) [BIX67, AVO77, STA81, NES96]. Rather than being sought out as sources of unique information, perturbations are generally given a wide berth by experimentalists. The reason for this is simple: a perturbation destroys the regular pattern of transition frequencies and intensities on which the assignment of a spectrum is based [LEF86]. A central theme of this project is the development of multispectral techniques and pattern-recognition methods that will enable experimentalists to record and interpret dynamically relevant spectra, regardless of the apparent complexity of these spectra.



A perturbation disrupts the pattern in an absorption or LIF spectrum. Dispersed Fluorescence (DF) spectroscopy, wherein one records the spectrum of the fluorescence that results when a single eigenstate in an LIF spectrum is excited, contains information that can reveal the identity of several of the electronic-vibration basis states present in the selected eigenstate [YAM91, SOL95, 96, ACE99, CUN00a].

There is a long history of observations and partial assignments of the low-J perturbers of the HCCH  $S_1$   $3v_3$   $K=1$  manifold [SCH86, UTZ93, DUP91, 93, 95b, OCH87, 91, WOL90, DRA94]. It is clear that at least five classes of basis state are involved: (i) the  $S_1$   $3v_3$  ( $v_3$  is the *trans-bend*) LIF-bright state, (ii) the  $S_1$   $4v_b$  class of LIF-dark but DF-bright anharmonic ( $4v_4$ ,  $2v_4 + 2v_6$ , and  $4v_6$ , where  $v_4$  is the torsion and  $v_6$  is the antisymmetric in-plane bend) and Coriolis ( $v_4 + 3v_6$  and  $3v_4 + v_6$ ) perturbors [UTZ93], (iii) the  $T_3$  *doorway* state, which is both LIF- and DF-dark [CUN00a], (iv) the  $T_1$  dark states [DRA94], and (v) high vibrational levels of  $S_0$  [DUP91, 93, 95b]. The DF spectrum from an unperturbed  $S_1$   $nv_3$  level is well known, from our DOE-supported project [YAM91, SOL95, 96, ACE99], to consist of a progression of *polyads*, each illuminated by a single *bright-state* (which involves excitation exclusively in the CC-stretch and *trans-bend* vibrations of  $S_0$ ). The two distinct patterns of frequencies and relative intensities within each polyad, generated by *either* a  $3v_3$  *or* a  $4v_b$  pluck, are known from the  $H^{eff}$  model that provides a complete picture of the IVR on the acetylene  $S_0$  potential surface [JAC99, CUN00a]. When the eigenstate from which the DF spectrum is recorded contains significant contributions from both  $3v_3$  and  $4v_b$  basis states, the observed intrapolyad pattern is a superposition of the  $3v_3$  and  $4v_b$  patterns. However, when the selected eigenstate contains  $T_3$ ,  $T_1$ , or  $S_0$  basis state character, the result is no distortion of either the intrapolyad or interpolyad patterns in the DF spectrum. The intensity pattern in our supersonic jet UV-LIF spectrum implies that the  $S_1$   $3v_3$  bright state primarily interacts with two ( $J = 1, 2$ , and  $3$ ) or three ( $J = 4$ ) dark states [CUN00a], Drabbels' higher resolution UV-LIF spectra [DRA94] show that each of these is fractionated into  $\sim 10$   $T_1$  quasi-eigenstates, and the Zeeman Anticrossing (ZAC [DUP91]) and Quantum Beat (ZQB [DUP93, 95b]) spectra show that each quasi-eigenstate is capable of interacting with as many as 100 dark  $S_0$  states. Our DF spectra show that the  $S_1$   $3v_3$  bright state and the  $T_3$  *doorway* state cross at  $J_c = 3$  and that the level crossing between  $3v_3$  and  $4v_b$  occurs at  $J_c < 1$ . Rotational constants and perturbation matrix elements are also determined [ALT00b, CUN00a].

**Figure 8.** The  $S_1$   $3v_3$  bright state is perturbed by  $T_3$  and by  $S_1$   $4v_b$  and at least one other unidentified state. The labels T, M, and E refer respectively to triplet ( $T_3$ ), main ( $S_1$   $3v_3$ ), and extra ( $S_1$   $4v_b$ ).



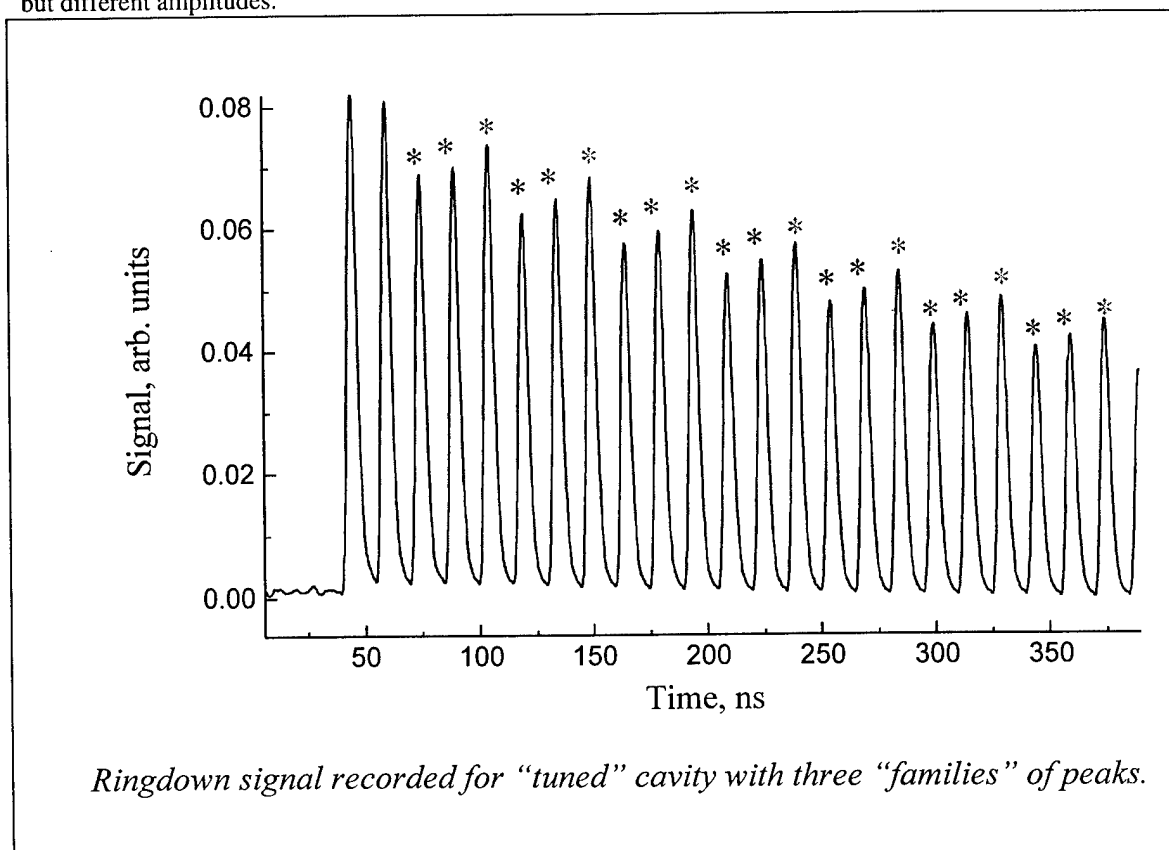
The DF results [CUN00a] confirm our statistical analyses of our SEELEM and UV-LIF spectra [ALT00a] and our L-K analysis of Drabbels' high-resolution UV LIF spectra [ALT00b]. They also explain the plateau intensity pattern observed in our UCSB SEELEM spectra [HUM97]. The plateau is the result of a quantum interference effect. The interference switches from constructive to destructive at  $J=3$  because of a sign-reversal of the  $S_1 \sim T_3$  mixing coefficients at  $J_c$ . The eigenvectors of our  $T_3 \sim 3v_3 \sim 4v_b$  3-state fit

model confirm an essential qualitative feature of our ISC model. The  $T_3$  *doorway* state interacts primarily with the  $S_1$   $3v_3$  *bright* state but is prohibited, by poor Franck-Condon overlap, from interacting with the  $S_1$   $4v_b$  perturber. Therefore the fractionation (into the  $\sim 10$  state per  $\text{cm}^{-1}$  manifold of  $T_1$  *dark* states) of each feature in the UV-LIF spectrum [DRA94] correlates with the fractional  $T_3$  *doorway* state character in that feature: the nominal  $T_3$  feature is most fractionated and the nominal  $S_1$  perturber feature is least fractionated. This is *mode-specific* ISC!

This is mechanism, not phenomenology. There is a Franck-Condon reason why a special class of *doorway* state is effective in initiating the nonradiative decay of each class of *bright* state.

## 6. UV Cavity Ringdown.

We plan to exploit the exceptional sensitivity and simplicity of Cavity Ring-Down Spectroscopy (CRDS) [OKE95, ZAL95, LEH96, HAG98] for direct observation of the  $T_1 \leftarrow S_0$  absorption spectrum. However, in the  $\lambda < 300$  nm UV region, mirrors with reflectivity greater than 99.8% are either unavailable or prohibitively expensive. In a DOE-supported project we have implemented a CRDS scheme that closely approaches the quantum noise limit ( $N^{0.5}$  where  $N$  is the number of photons/pulse incident on the entrance mirror of the cavity) even when 99.5% reflective mirrors are used. The critical features of this scheme are (i) the length of the CRD cavity is chosen so that the output beams from the cavity sequentially illuminate three stationary spatial regions on the photodetector surface and (ii) our least squares fitting algorithm takes into account the existence of three families of exponentially decaying outputs that have the same decay rate but different amplitudes.



**Figure 9.** UV Cavity Ringdown. Owing to the different sensitivity of the three spots on the detector illuminated by the output beams from the ringdown cavity, there are three families of decay curves, each with the same exponential decay constant. The pulses inside the cavity are resolved because the 12 ns round trip time inside the 2m cavity is longer than the  $\sim 4$  ns pulse.

inside the cavity are resolved because the 12 ns round trip time inside the 2m cavity is longer than the ~4 ns pulse.

A crude estimate of the intensity of a direct  $T_i \leftarrow S_0$  absorption band is obtained from that of the corresponding  $S_1 \leftarrow S_0$  band [ING53, NAK64], multiplied by the fractional  $S_1$  character in  $T_i$  obtained using nondegenerate perturbation theory for the first-order correction to the wavefunction [LEF86]. The spin-orbit matrix element is taken as the spin-orbit coupling constant for the Carbon 2p orbital,  $\zeta = 29 \text{ cm}^{-1}$  and the energy difference between  $S_1$  and  $T_i$  states is taken as  $10,000 \text{ cm}^{-1}$ . Thus the fractional  $S_1$  character in  $T_i$  will be  $8 \times 10^{-6}$  and the strongest  $T_i \leftarrow S_0$  absorption band will therefore be on the order of  $10^5$  times weaker than the strongest  $S_1 \leftarrow S_0$  band. As practise for our first attempt at recording a  $T_1 \leftarrow S_0$  band by CRDS, we recorded the  $S_1 \leftarrow S_0$  origin band at  $\lambda = 236 \text{ nm}$ , which has a vibrational band oscillator strength of  $f = 2.5 \times 10^{-9}$ , a factor of ~700 smaller than that of the  $V^3_0$  (" $3v_3$ ")band [ING53, WAT95].

It will be interesting to compare the relative sensitivities and unique electronic-vibration basis state selectivities of IR-LIF, SEELEM, and CRDS for recording direct  $T \leftarrow S_0$  transitions.

## 7. Hg\* Photosensitization Experiments.

There is a long history in Organic Photochemistry [OKA78] of using Hg\* photosensitization [HUN71, BUR72, WEN79] to promote anti-Woodward-Hoffmann [WOO71] reactions. 253.7 nm radiation from a mercury lamp is used to excite Hg atoms from the  $^1S_0$  electronic ground state to the  $^3P_1$  excited state that in turn is efficiently transferred into the long-lived  $^3P_0$  state by collisions with a nonreactive gas such as  $N_2$ . The photosensitized reaction is carried out in a quartz tube that contains a trace amount of Hg (1 mTorr), a high pressure of  $N_2$  (1 atm), and the organic reagents (~10 Torr). Efficiencies near 100% for transferring the excitation from Hg ( $^3P_1$ ) to Hg ( $^3P_0$ ) to the unsaturated organic reagent are typically claimed [WEN79].

Preliminary gas cell experiments demonstrate the feasibility of a lower pressure implementation of the Hg\* photosensitization scheme. Direct laser excitation in the blue wing of the Hg  $^3P_2 \leftarrow ^1S_0$  or  $^3P_0 \leftarrow ^1S_0$  atomic transition, in the presence of 100 Torr of Xe, results in a large and spatially uniform population of long lived (~1 ms)  $^3P_2$  or  $^3P_0$  Hg atoms, respectively [OHM94, 95, 99, KUR98]. The populations in the  $J = 0, 1$ , or 2 fine structure levels of the Hg  $^3P_J$  state are monitored by laser excitation of the  $^3S_1 \leftarrow ^3P_J$  atomic transition, which results in visible  $^3S \rightarrow ^3P$  and UV  $^3P_1 \rightarrow ^1S$  fluorescence.

Our plan is to use Hg\* photosensitization to populate metastable states of several small molecules, starting with NO and acetylene. The goal is to develop an Intracavity Laser Absorption Spectroscopy (ICLAS) scheme for monitoring populations in metastable electronically excited states of molecules [ICL00]. ICLAS is a versatile, absorption-based scheme, with sensitivity comparable to CRDS, but with two crucial advantages over CRDS: it is a multiplex scheme, capable of simultaneously recording several tens of  $\text{cm}^{-1}$  of spectrum at  $0.02 \text{ cm}^{-1}$  resolution, and, in a double-sampling scheme recently implemented by Kachanov in the Steinfeld lab at MIT, ICLAS can be used to monitor kinetic processes at a few microseconds time resolution. The MIT ICLAS setup, the result of a DURIP grant to Steinfeld and Field, is based on a Ti:sapphire intracavity gain medium. The lasing range of Ti:sapphire, 700-1100 nm, is a nearly perfect match for a class of electronic transitions that is ideally suited for monitoring the populations in metastable electronic states. For almost all unsaturated H, C, N, O molecules, the  $\pi^* \leftarrow \pi$  or  $\pi^* \leftarrow n$  metastable excited state can be monitored via a  $\pi \leftarrow \sigma$  or  $n \leftarrow \sigma$  electronic transition in the red to near-IR region.

## 8. Collaborations at AFRL, Hanscom Research Site: Pattern Recognition and Baseline Stripping.

As a result of reciprocal visits by Steven Lipson to MIT and Robert Field and Matt Jacobson to the AFRL Hanscom Research Site, several collaborative projects involving pattern-recognition techniques were initiated. Initial results have been reported in two papers [JAC98, RUC00] and seven conference abstracts [VIT97a-g].

In the first paper [JAC98], Hybrid Linear Pattern Analysis (HLP) was used to extract information from atmospheric emission simulation experiments conducted in the LABCEDE facility of the Hanscom Research Site. HLP combines model-based and model-free pattern-recognition techniques. A pulsed electron beam excites CO in a cryogenic chamber and time resolved IR spectra are recorded. The spectra contain information about the vibrational populations and collisional deactivation rates in CO X  $^1\Sigma^+$   $v=0-12$ . Severe self-absorption in the  $1 \rightarrow 0$  band prohibits the use of a model-based least-squares fit to the time-resolved spectra. The initially unknown pattern associated with the  $1 \rightarrow 0$  band is recovered by the extended spectral cross-correlation method (XCC) [JAC97, COY97] by assuming that the spectral profile of this pattern does not change with time. All of the other vibrational bands are free of distortion by self-absorption, thus their band profiles can be modeled by standard least squares fitting techniques. HLP recovers the time-dependent populations in all vibrational levels  $v = 1-12$  and the time varying spectral profile of the  $1 \rightarrow 0$  band in a single, statistically rigorous fit [JAC98]. This paper was named the AFRL Space Vehicles Directorate "Team Publication of the Year" for 2000.

The second paper [RUC00] addresses the classic problem of separating baseline from signal. This becomes an even more important problem when one begins to apply model-free pattern-recognition techniques (e.g. XCC and XAC) to a data stream where the nature and number of patterns to be extracted are initially unknown. Since the model-free techniques begin with a *recursion map* [JAC97, COY97], which is a plot of the intensities in one data record vs. those in another, it is essential to partition the measured intensities into spurious baseline and real signal contributions. Baseline corrupts patterns and vitiates the effectiveness of any pattern-recognition procedure. This collaboration, between an Australian statistician Andreas Ruckstuhl, James Dodd from AFRL, and the MIT group, materialized at a mini-symposium organized by the P. I. on Modern Spectroscopic Techniques at the 1998 American Chemical Society National Meeting in Boston.

A technique entitled Robust Baseline Extraction (RBE) is introduced, which uses techniques of robust local regression to estimate baselines in spectra that consist of sharp features superimposed upon a continuous, slowly varying baseline [RUC00]. The technique is applied to synthetic spectra, to evaluate its capabilities, and to laser-induced fluorescence spectra of OH (produced from the reaction of ozone with hydrogen atoms). The latter example is a particularly challenging case for baseline estimation because the experimental noise varies as a function of laser frequency. RBE enabled Dodd et al [DOD00] at the AFRL Hanscom Research Site to obtain rapid-scan records of OH LIF data by scanning slowly near lines and fast between lines.

Similar pattern-recognition methods were developed by other members of the Lipson group and applied to hyper-spectral (one spectrum for each of an enormous number of spatial locations) problems, such as target recognition and the IR spectra of the Earth's atmosphere recorded by the CIRRUS 1A instrument aboard the Space Shuttle [VIT97a-g].

## 9. The Spectroscopic Signature of Bond-Breaking Isomerization in HCP.

One of the classic problems in spectroscopy and molecular dynamics is: “what happens to the quantum spectrum and to classical trajectories when bond-breaking isomerization becomes energetically accessible?” The naïve expectation was that spectra would become uninterpretable complex and that trajectories would become chaotic. Even though HCP corresponds to a saddle-point rather than a local minimum on the HCP  $S_0$  potential energy surface (PES), the HCP  $\leftrightarrow$  HPC system has emerged as the simplest and best understood (experimentally and theoretically) bond-breaking isomerizing system [HCP99].

The HCP project [LEH85] began at Princeton and was joined at MIT in 1989 as an AFOSR-supported Simulated Emission Pumping (SEP) study of vibrationally highly excited levels of the HCP  $X \sim {}^1\Sigma^+$  electronic ground state [CHE90a]. A postdoc, Dr. Haruki Ishikawa [ISH96] made critical progress in the interpretation of the SEP spectra. When Dr. Ishikawa returned to Tohoku University, a long term MIT-Tohoku collaboration was established [HCP99]. The experimental part of the HCP project and the fitting of all spectra to Ishikawa’s polyad  $H^{\text{eff}}$  model were transferred to Prof. Ishikawa’s laboratory. Since then several theorists have joined the collaboration (Reinhard Schinke, Stavros Farantos, Marc Joyeux, Michael Kellman, Alejandro Frank and Renato Lemus). They computed a refined *ab initio* PES, calculated wavefunctions and spectroscopic properties of the eigenstates of the PES, examined the nodal structure of these eigenstates, calculated classical trajectories, and subjected the trajectories to the diagnostics of nonlinear classical dynamics [BEC97].

One of the most remarkable things to emerge is that the standard, spectroscopically determined,  $H^{\text{eff}}$  matrix model contains all of the qualitative changes in spectral patterns, nodal structures, and classical trajectories [HCP99]. Somehow the  $H^{\text{eff}}$  “knows” the minimum energy isomerization path on the PES! To a very good approximation, even in the energy region of the top of the isomerization barrier, polyads still exist, even though the clustering of vibrational eigenstates into closely spaced polyad groups of levels no longer exists. At high energy the polyads begin to overlap each other, but the inter-polyad matrix elements between the lowest members of a higher energy polyad and the highest members of a lower energy polyad start out very small. This means that the polyad model generates the essential information that ensures its bootstrapping extension into higher energy regions where interpolyad interactions are locally severe but globally modest.

Spectroscopists observe spectra. They cannot directly view wavefunctions, thus their spectroscopic assignments cannot be guided by the nodal structures of observed eigenstates. Their assignments are based on patterns of energy levels and relative intensities, and these assigned levels are the bricks and mortar from which an  $H^{\text{eff}}$  matrix model is built. This model is a better tool, than *anyone* would have imagined, for predicting and describing unimolecular dynamics, extracting useful information from changes in spectral patterns as the isomerization region is approached, and generating classical trajectories in a *reduced-dimension* space that is much better suited than the exact Hamiltonian to the visualization diagnostics of nonlinear dynamics [HCP99, ACE99].

This study of HCP is the best possible illustration of how the central tool of the molecular spectroscopist, the  $H^{\text{eff}}$  matrix model, facilitates extraction of **causal mechanisms for dynamics** from spectra of extreme complexity.

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- VIT97a. "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the University of Virginia Physics Department Atomic and Molecular Seminar (Charlottesville, VA, April 1997) - Invited
- VIT97b. "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the 1997 Spring Meeting of the American Geophysical Union (Baltimore, MD, May 1997)
- VIT97c. "Disentangling Vibrational Bands in CO Spectra Utilizing Spectroscopic Pattern Recognition Techniques" M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, and P.S. Armstrong, Presented at the 52nd International Symposium on Molecular Spectroscopy (Columbus, OH, June 1997)
- VIT97d. "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the 20th Annual Review Conference of Atmospheric Transmission Models (Hanscom AFB, MA, June 1997)
- VIT97e. "Techniques for Target Detection Using Hyperspectral Data" C. L. Allred, D.L. Vititoe, S.J. Lipson, R.B. Lockwood, L. S. Jeong, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, R.W. Field, and W.J. Marinelli, Presented at the Spectral Imaging Technology Workshop (Kirtland AFB, NM, August 1997)

- VIT97f. "Techniques for Target Detection Using Hyperspectral Data" D.L. Vititoe, C. L. Allred, S.J. Lipson, R.B. Lockwood, L. S. Jeong, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field Presented at the Defense Intelligence Agency Advanced Concepts Division 1997 Spectroradiometric Symposium (San Diego, CA, November 1997)
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### III AFOSR Supported Publications (since 1996).

- H. Ishikawa, Y.-T. Chen, Y. Ohshima, B. Rajaram, J. Wang, and R. W. Field, "Stimulated Emission Pumping Spectroscopy of HCP near the Isomerization Barrier:  $E_{VIB} \leq 25,315 \text{ cm}^{-1}$ ", J. Chem. Phys. **105**, 7383-7401 (1996).
- R. W. Field, J. P. O'Brien, M. P. Jacobson, S. A. B. Solina, W. F. Polik, and H. Ishikawa, "Intramolecular Dynamics in the Frequency Domain," Adv. in Chem. Phys. **101**, 463-490 (Solvay Conference 1995), 1997.
- S. Drucker, J. P. O'Brien, P. Patel, and R. W. Field, "The Effects of Triplet Perturbers in Photophysical Processes in the  $A^1A_u$  state of Acetylene," J. Chem. Phys. **106**, 3423-3426 (1997).
- H. Ishikawa, Chioko Nagao, Naohiko Mikami, and R. W. Field, "Observation of the 'Isomerization States' of HCP by Stimulated Emission Pumping Spectroscopy: Comparison between Theory and Experiment," J. Chem. Phys. **106**, 2980-2983 (1997).
- S. J. Humphrey, C. G. Morgan, A. M. Wodtke, K. L. Cunningham, S. Drucker, and R. Field, "Laser Excited Metastable States of Acetylene in the 5.5-5.7eV Region," J. Chem. Phys. **107**, 49-53(1997).

M. P. Jacobson, S. L. Coy, and R. W. Field, "Extended Cross-Correlation: A Technique for Spectroscopic Pattern Recognition," J. Chem. Phys. 107, 8349-8356 (1997).

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M. P. Jacobson, S. L. Coy, R. W. Field, S. J. Lipson, R. B. Lockwood, D. L. Vitito, W. A. M. Blumberg, and P. S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments," J. Phys. Chem. 104, 249 - 257 (2000).

H. Ishikawa, R. W. Field, S. C. Farantos, M. Joyeux, J. Koput, C. Beck, and R. Schinke, "HCP→CPH Isomerization: Caught in the Act!," Annu. Revs. Phys. Chem. 50, 443-484 (1999).

M. Joyeux, D. Sugny, V. Tyng, M. E. Kellman, H. Ishikawa, R. W. Field, C. Beck, and R. Schinke, "Semiclassical Study of the Isomerization States of HCP," J. Chem. Phys. 112, 4162-4172 (2000).

A. F. Ruckstuhl, M. P. Jacobson, R. W. Field, and J. A. Dodd, "Baseline Subtraction Using Robust Local Regression Estimation," J. Quant. Spectr. Radiat. Transf. 68, 179 - 193 (2001).

S. Altunata and R. W. Field, "A Statistical Approach to the Study of Singlet-Triplet Interactions in the 5.5 - 5.7 eV Region of Acetylene, J. Chem. Phys. 113, 6640 - 6651 (2000).

#### IV. Interactions/Transitions: Talks

##### Talks.

Several talks were given by Robert Field in which the XCC techniques was applied to Dispersed Fluorescence Spectra of C<sub>2</sub>H<sub>2</sub>. The C<sub>2</sub>H<sub>2</sub> DF project is supported by DOE, but the development of XCC was primarily supported by AFOSR .

8/25/96	American Chemical Society, Invited Talk, "Core-Nonpenetrating Rydberg Series: Spectroscopic Black Holes."
10/24/96	Optical Society of America, Invited talk, "Now Wrinkles on an Old Plum: Frequency-Modulator Enhanced Magnetic Rotation and Pulsed Frequency Modulation Spectroscopies."
11/6/96	Discussion Meeting of the Royal Society: Molecular Rydberg Dynamics, Invited talk, "Core-Nonpenetrating Rydberg Series. Spectroscopic Black Holes."
11/18-22/96	Three talks, Princeton University, Department of Chemistry  "HCP↔HPC Isomerization: Caught in the Act"  "Acetylene Unzipped: Dynamics from Frequency-Domain Dispersed Fluorescence Spectra"  "Spectroscopic Black Holes"
12/3/96	University of Connecticut, Department of Physics, "Acetylene Unzipped"

- 1/7/97 Gordon Research Conference, Molecular Energy Transfer, Ventura, CA, "Intramolecular Dynamics in the Frequency Domain"
- 1/16/97 Rowland Institute, "Spectroscopic Black Holes"
- 4/19-5/4/97 Tsinghua University, Beijing, five lectures.
- 6/3/97 Invited Talk, Canadian Society for Chemistry, Windsor, Ontario. "Acetylene Unzipped."
- 6/16-20/97 52nd International Symposium on Molecular Spectroscopy
- RA09 Robert W. Field, "A Dispersed Fluorescence Data Set for the  $\tilde{X}$ -State of Acetylene: An Approach Toward Multidimensional Vibrational Spectroscopy."
- RA10 Matthew Jacobson, "Analysis of Acetylene  $\tilde{X}$ -State Dynamics Utilizing Spectroscopic Pattern Recognition Techniques."
- RA11 Matthew P. Jacobson, "Disentangling Vibrational Bands in Infrared Spectra of CO by Utilizing Spectroscopic Pattern Recognition Techniques" (with Steven J. Lipson, Ronald B. Lockwood, David L. Vittoe, William A.M. Blumberg, and Peter S. Armstrong)
- RI01 Kevin Cunningham, "Laser Excited Metastable Spectroscopy of C<sub>2</sub>H<sub>2</sub>"
- RI02 Robert W. Field, "Gateway Mediated Intersystem Crossing in C<sub>2</sub>H<sub>2</sub>"
- 7/11/97 Laboratoire Photophysique Moléculaire, Orsay, France, "Acetylene Unzipped."
- 10/13/97 CNRS Symposium in honor of Hélène Lefebvre-Brion, Orsay, France. "Perturbations Are Not Accidents," R. W. Field.
- 4/16/98 University of Pennsylvania, "Dispersed Fluorescence Spectra of Acetylene: Order Out of Chaos," R.W. Field.
- 5/1/98 Institute for Theoretical Atomic and Molecular Physics, "Large Amplitude Bending Dynamics of Acetylene," M.P. Jacobson.
- 6/15-19 53rd International Symposium on Molecular Spectroscopy, Ohio State University, Talks MI09, MI10, TB03, TG12, TG13, RF06, RF09, RF10.
- "Mode Beats and the Sensitivity Limit of the Pulsed Cavity Ring-Down Spectroscopy," A. A. Kachanov, S.I. Panov, I. Dubinsky, L.M. Ruslen, M.L. Silva, and R.W. Field.
- "An Optimal Data Acquisition Scheme for a Pulsed Cavity Ring-Down Experiment," A.A. Kachanov, S.I. Panov, I. Dubinsky, L.M. Ruslen, M.L. Silva, and R.W. Field.
- "The Predissociation Mechanism for  $2\Sigma^+$  Rydberg States of CaCl," J.O. Clevenger, N.A. Harris, R.W. Field, Jian Li.
- "Surface Electron Ejection by Laser-Excited Metastable Spectroscopy of C<sub>2</sub>H<sub>2</sub>," S.A. Altunata, K.L. Cunningham, S. Drucker, C.G. Morgan, and R.W. Field.

"Gateway Mediated Intersystem Crossing in C<sub>2</sub>H<sub>2</sub>," K.L. Cunningham, S. Drucker, S. Altunata, C.G. Morgan, and R.W. Field.

"Spectroscopic Investigation of the Generation of 'Isomerization' States of HCP: Eigenvector Analysis of the Bend-CP Stretch Polyad," H. Ishikawa, C. Nagao, N. Mikami, and R.W. Field.

"Rovibrational Level Structure of Acetylene by Stimulated Emission Pumping: Coriolis Coupling between  $\nu_2 + 4\nu_4$  and  $7\nu_4$ ," D.B. Moss, R. Duan, M.P. Jacobson, J.P. O'Brien, and R.W. Field.

"Large Amplitude Bending Dynamics of Acetylene," M.P. Jacobson, J.P. O'Brien, R.J. Silbey and R.W. Field.

8/23-27/98      216th National ACS Meeting, Boston, MA.

Symposium: Special Topics in High-Resolution Spectroscopy: Patterns in Spectra. R.W. Field and K.K. Lehmann co-organized 7 half-day sessions.

Talk #372      "Acetylene Pure Bending Dynamics," M.P. Jacobson, J.P. O'Brien, R.J. Silbey, and R.W. Field.

Talk #376      "Surface Electron Ejection by Laser-Excited Metastable Spectroscopy of Acetylene," K.L. Cunningham, S. Altunata, S. Drucker, C.G. Morgan, and R.W. Field.

Talks by R. Field, K. Cunningham, and S. Altunata at the 52nd (1997), 53rd (1998), 54th (1999), and 55th (2000) "International Symposium on Molecular Spectroscopy (Ohio State University)"

Talk by Selen Altunata at Wesleyan University (2000)

Talks by Robert Field at national ACS meetings (Spring, 2000 and Pacificchem 2000), Edwards Air Force Base (Spring, 2000), International Conference on Photochemistry (San Juan, Puerto Rico, April, 2000), Kobe University (May, 2000), Argonne National Lab (October, 2000), University of California, Riverside (December, 2000).

## V.      New Discoveries, Inventions, Patents.

None.

## VI.      Honors

Robert Field:      William F. Meggers Prize, Optical Society of America, October 22, 1996  
Doctor of Science (honoris causa), Amherst College, June 24, 1997.

Matt Jacobson:      Rao Prize, 52nd International Symposium on Molecular Spectroscopy.

Robert Field:      Elected to Fellowship in the American Academy of Arts and Sciences, 1998.

Robert Field:      Haslam and Dewey Professorship, 1999.

Susan Lang:      Dreyfus Undergraduate Research Fellowship, 1997.

Susan Lang: Chemistry Department Prize for Undergraduate Research, 1999.